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Abstract: A new carbon family with a prism structure has been found by quantum chemical calculations. The prism-C_20 has a D_10h structure with double-layered decagonal rings connected each other by ten vertical CC bonds. The CC bond lengths are 0.144 nm on the decagonal rings and 0.148 nm on the side faces. The diameter of the ring is 0.465 nm. The $prism - C_20$ is expected to be stable, since the lowest energy barrier from it was estimated to be 158.0 kJ mol1.

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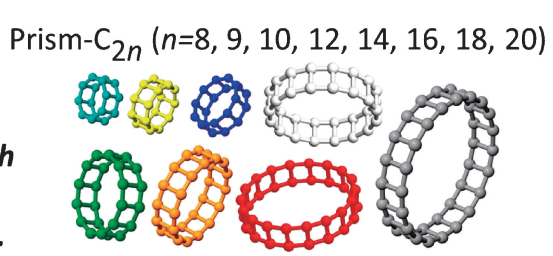
Editor's Choice

A Prism Carbon Molecule C_{20}

Koichi Ohno,*[1,2,3] Hiroko Satoh,[2,4] and Takeaki Iwamoto[1]
[1]*Department of Chemistry, Graduate School of Science, Tohoku University, Aramaki, Aoba-ku, Sendai, Miyagi 980-8578*
[2]*National Institute for Informatics (NII), Chiyoda-ku, Tokyo 101-8430*
[3]*Institute for Quantum Chemical Exploration, Minato-ku, Tokyo 108-0022*
[4]*Department of Chemistry, University of Zurich, 8057 Zurich, Switzerland*

(E-mail: ohnok@m.tohoku.ac.jp)

A new carbon family with a polygon prism structure, which looks like a hamster wheel.



A new carbon family with prism-C_{2n} structures ($n = 8$, 9, 10, 12, 14, 16, 18, and 20) has been found by quantum chemical calculations. The prism-C_{20} has a D_{10h} structure with double-layered decagon rings connected to each other by ten CC bonds, and it is expected to be stable, because the lowest energy barrier was estimated to be 158.0 kJ mol^{-1}.

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[1]*Department of Chemistry, Graduate School of Science, Tohoku University, Aramaki, Aoba-ku, Sendai, Miyagi 980-8578*
[2]*National Institute for Informatics (NII), Chiyoda-ku, Tokyo 101-8430*
[3]*Institute for Quantum Chemical Exploration, Minato-ku, Tokyo 108-0022*
[4]*Department of Chemistry, University of Zurich, 8057 Zurich, Switzerland*

(E-mail: ohnok@m.tohoku.ac.jp)

A new carbon family with a prism structure has been found by quantum chemical calculations. The prism-C_{20} has a D_{10h} structure with double-layered decagonal rings connected each other by ten vertical CC bonds. The CC bond lengths are 0.144 nm on the decagonal rings and 0.148 nm on the side faces. The diameter of the ring is 0.465 nm. The prism-C_{20} is expected to be stable, since the lowest energy barrier from it was estimated to be 158.0 kJ mol^{-1}.

Carbon is a ubiquitous element that composes various substances. Simple substances made of carbon include diamond, graphite, and some other allotropes such as fullerenes,[1] carbon nanotubes,[2] and graphenes.[3] These carbon families consist mostly of hexagonal rings at their CC bond networks; fullerenes and carbon nanotubes partly include pentagons in addition to hexagons. In view of the existence of various sizes of hydrocarbons such as cycloalkanes and annulenes as well as prismanes, a new class of carbon family other than penta-/hexagonal networks may exist.

In the present study, theoretical explorations of new carbon substances were performed, and herein we report a C_{20} molecule with a prism structure **1** shown in Figure 1. It has a D_{10h} symmetry of double layered ten-membered planar rings (regular decagon rings) connected to each other by ten vertical CC bonds on the side faces, in which there are only two types of CC bonds: of bond length 0.144 nm on the ten-membered rings and of bond length 0.148 nm on the sides, which are mutually orthogonal. The diameter of the C_{10} ring is 0.465 nm.

The prism structure **1** has been found in the context of the explorations of chemical structures, starting with C_4H_4 and C_6H_4. Quantum chemical calculations were performed for the ground singlet state by Gaussian 09.[4] Theoretical explorations of chemical structures on potential energy surfaces (PES) of the ground singlet state were made by the GRRM method.[5] A full anharmonic downward distortion following (ADDF) search for C_4H_4 at the level of B3LYP/6-31G* gave 32 equilibrium structures (EQ) and 171 transition structures (TS). The global minimum of C_4H_4 is vinylacetylene (EQ0). The second lowest is cumulene (EQ1, D_{2h}: at 8.0 kJ mol^{-1} with respect to EQ0). The third is methylenecyclopropene (EQ2, C_{2v}, 85.3 kJ mol^{-1}), and the forth is cyclobutadiene (EQ3, D_{2h}, 153.2 kJ mol^{-1}), which is much lower than tetrahedrane (EQ15, T_d, 255.0 kJ mol^{-1}). A limited ADDF search[6] with a parameter of LADD = 5 for C_6H_4 at the level of B3LYP/6-31G* yielded 356 EQs and 1061 TSs. The global minimum of C_6H_4 is *o*-benzyne (1,2-didehydrobenzene, EQ0, C_{2v}), and the second is *m*-benzyne (bicyclo[3.1.0]-hexa-1,3,5-triene, EQ1, C_{2v}, 46.7 kJ mol^{-1}). The third is vinyl diacetylene (EQ2, C_1, 48.0 kJ mol^{-1}), and the forth is 1,2,3,4,5-hexapentaene (EQ3, D_{2h}, 70.4 kJ mol^{-1}). The lowest cyclic isomer is 1,1-didehydrofulvene (EQ8, C_{2v}, 129.2 kJ mol^{-1}), and *p*-benzyne (1,4-didehydrobenzene, EQ11, D_{2h}) appears at 162.8 kJ mol^{-1}. The lowest bicyclic isomer other than *m*-benzyne analogues is butalene (bicyclo[2.2.0]hexa-1,3,5-triene, EQ22, D_{2h}, 240.3 kJ mol^{-1}).

Out of the 32 EQs obtained for C_4H_4, 14 EQs contain three- or four-membered rings. In the case of C_6H_4, many EQs include rings of 3–6 carbon atoms. In the present study, we focused our attention on the following structures with four-membered rings in Figure 2, cyclobutadiene **2** and butalene **3**, because four-membered rings look to be stable enough to form ladder structures.

Hence, we tried to optimize a longer ladder structure of $C_{10}H_4$ with many squares, and a curved C_{2v} structure **4** in Figure 3 was obtained from a planar initial structure. Such curved ladder C_{2v} structures similar to **4** were reported for $C_{2n}H_4$ (n = 5–10) as condensed cyclobutadienoids by Sakai and co-workers.[7] Here, the presence of terminal hydrogens tends to shorten the terminal vertical CC bonds and also to make the shape of the longer carbon chains irregular. Since connecting a

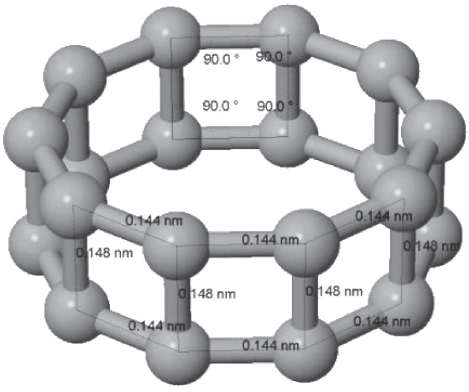

Figure 1. D_{10h} structure of prism-C_{20} **1**. Two decagon rings are connected with ten vertical CC bonds on the side faces.

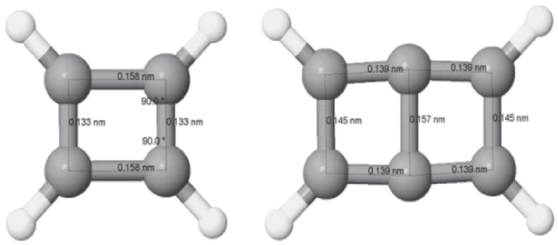

Figure 2. Cyclobutadiene **2** (left) and butalene **3** (right).

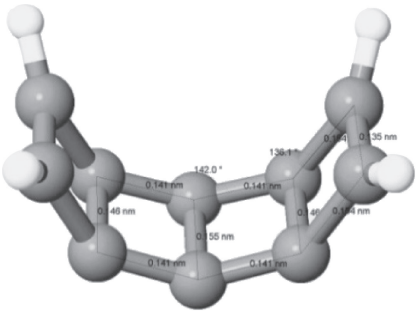

Figure 3. A condensed cyclobutadienoid $C_{10}H_4$ **4**.

pair of the curved ten-carbon ladders at the terminal hydrogens most likely produces a circular ladder structure, just like a hamster wheel, we went for further optimization and obtained the D_{10h} structure of the prism-C_{20} **1** in Figure 1. All Hessian eigenvalues for **1** were found to be positive and to give confirmation of the minimum structure. Geometrical reoptimization calculations for the ground singlet state were performed at higher levels, B3LYP/6-311++G(d,p), B3LYP/6-311++G(2d,2p), B3LYP/cc-pVDZ, and B3LYP/cc-pVTZ, for which equilibrium geometries were found to be the same within three digits as those at the level of B3LYP/6-31G*.

Concerning the levels of calculations, ab initio CASSCF, CCSD(T) MO method, and the B3LYP density functional method with a 6-31G* basis set were compared for $C_{2n}H_4$ ($n = 2$–5);[7] the determined geometries were well generated even at the B3LYP level, and geometrical parameters were qualitatively the same in the three methods. Hence, in the following discussion, we will use our B3LYP results to investigate various aspects of D_{10h}-prism-C_{20} **1**.

It is well known that there are many isomeric forms for C_{20} clusters.[8–14] Relative energies of distinct isomers, such as cage (fullerene type), bowl, and ring forms, have been extensively studied. The geometry optimization of a cage structure initiated with a regular dodecahedron underwent symmetry-lowering due to the Jahn–Teller effect, resulting in considerable discrepancies from the ideal shape of I_h.[11] The energy of **1** was determined to be 12.72 eV (1227 kJ mol^{-1}) with respect to the energy of an optimized monocyclic ring form **5** at the level of B3LYP/6-31G*, which can be compared with the energies of various types of C_{20} clusters in the previous study (2.9–14.7 eV).[12]

The monocyclic ring structure **5** shows alternate CC bond lengths of 0.124 and 0.135 nm (Figure 4), which correspond well with typical triple and double bonds. In the case of **1**, the bond lengths are 0.144 nm on the ten-membered rings and 0.148 nm on the side faces, which are shorter than the typical single bond of 0.154 nm. Considering decagons satisfy the $4n + 2$ rule, it follows that the C_{10} rings form a conjugated system and the common length of the side CC bonds can be ascribed to the resonance behavior in the C_{10} rings. The HOMO level of **1** is at 6.286 eV, and the HOMO–LUMO gap is 2.919 eV. These values are located in interesting regions in comparison with those for fullerenes and graphenes.[15]

In order to confirm the property of chemical bonds, bondpaths, as defined in a QTAIM (Quantum Theory of Atoms in Molecules)[16] molecular graph (Figure 5), were obtained using AIM2000.[17] Figure 5a shows that the carbon atoms are

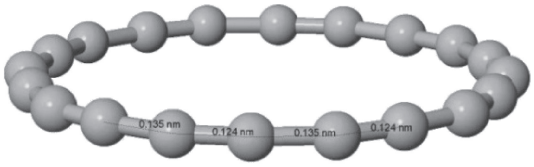

Figure 4. Monocyclic C_{20} **5**.

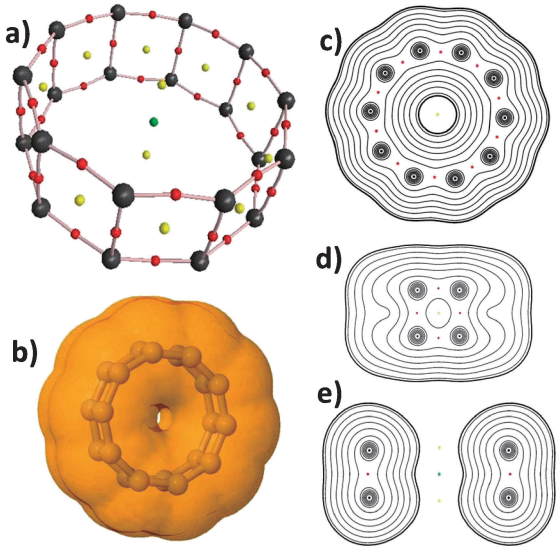

Figure 5. a) Bondpaths and electron-density critical points of the prism-C_{20}. b) The van der Waals surface. c) Electron density contours for the ring plane. d) Electron density contours for the square shape including the neighboring side bonds. e) Electron density contours for the cutting plane including the central symmetry axis and four carbon atoms.

connected by bondpaths with bond-critical points (BCP) shown as red balls. Electron densities on the BCPs are 0.2700 au on the ring bonds and 0.2688 au on the side bonds, which are normal values for ordinal chemical bonds. Electron densities on the other points are much smaller; ring critical points (RCP) marked as yellow balls at the centers of squares show a density of 0.1090 au, RCPs at the center of big rings show a density of 0.0012 au, and a cage critical point (CCP) marked as a green ball at the body center has a very low density of 0.00077 au.

The van der Waals surface is shown in Figure 5b. The size of **1** can be estimated from its diameter of 0.465 nm and the side bond length of 0.148 nm as well as the van der Waals radii of carbon, 0.17 nm. The thickness of the van der Waals envelope of C_{20} is 0.488 nm, the outer diameter is 0.807 nm, and the inner diameter of the hole is 0.127 nm. The size of the inner hole seems too small for repulsive particles, but it may capture some positive ions with attractive forces.

Figure 5 also shows electron density contours for the ring plane (c), the square plane (d), and the cutting plane (e). The outer thick curves at the density of 0.004686 au indicate the molecular surface corresponding to the van der Waals surface. The contour curves are shown at $\rho = a \times 2^n$, where $a =$ 0.00625 au and $n = 0, 1, 2, \ldots$. BCP, RCP, and CCP are also shown in Figures 5c–5e. The doughnut hole of the molecular surface can be recognized in Figures 5b, 5c, and 5e.

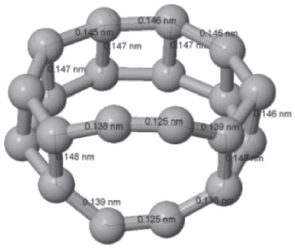

Figure 6. Deformed prism C_{20} **6**.

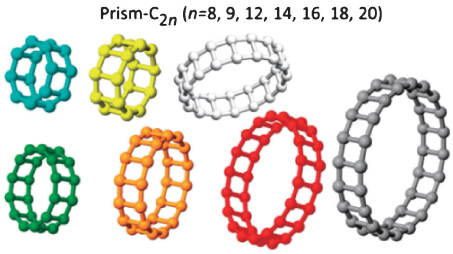

Figure 7. C_{16}, C_{18}, C_{24}, C_{28}, C_{32}, C_{36}, and C_{40} of the prism carbon family confirmed by B3LYP/6-31G* calculations.

We studied reaction channels around the D_{10h} structure **1** by the GRRM method.[5] The lowest reaction pathway has a barrier of 158.0 kJ mol^{-1} (1.638 eV) after ZPVE corrections, through which the central two side-bonds in three fused square rings are removed from **1** to produce a deformed (C_2) double decagon ring structure **6** (Figure 6), which consists of a side octagon composed of double–triple–double CC bond chains fused with the decagon rings and two side CC bonds.

The bond-breaking propensity at the four-membered rings is consistent with the superior stability of the decagon rings. It is to be noted that the double–triple–double CC bond moiety of **6** is very similar to the bond-alternating chain of the monocyclic C_{20} ring structure **5**. The lowest energy barrier (1.638 eV, 158.0 kJ mol^{-1}) is much larger than thermal energies, which indicates the thermal stability of **1**; the prism-C_{20} **1** comprising such an enormous energy of 12.72 eV (1227 kJ mol^{-1}) may possibly behave as a chemical energy reservoir.

Further quests of the structures of the prism carbon family were made for C_{2n} ($n = 6$, 7, 8, 9, 10, 12, 14, 16, 18, and 20) by B3LYP/6-31G* calculations. Prism carbons were found for $C_{12}(C_{3v})$, $C_{14}(C_s)$, $C_{16}(D_{8h})$, $C_{18}(D_{3h})$, $C_{20}(D_{10h})$, $C_{24}(D_{4h})$, $C_{28}(D_{14h})$, $C_{32}(C_{8v})$, $C_{36}(C_{2h})$, and $C_{40}(D_{20h})$. Some prism carbons other than C_{20} are shown in Figure 7. It is interesting that in the case of C_{16}, C_{20}, C_{28}, and C_{40} the C_n rings are regular polygons with the same CC bond lengths, but in other cases the top and the bottom rings are slightly deformed from the regular polygons. Geometric parameters of the studied structures C_{2n} are contained in Supporting Information.[18]

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Supporting Information is available electronically on J-STAGE.

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